Construction Materials and Structures
S.O. Ekolu et al. (Eds.)
IOS Press, 2014

doi:10.3233/978-1-61499-466-4-718

Effects of multi-walled carbon nanotubes on strength and interfacial transition zone of concrete

P. Van TONDER[1] and T.T. MAFOKOANE
Department of Civil Engineering Science, University of Johannesburg

Abstract. Multi-walled carbon nanotubes (MWCNTs) were used to try and eliminate the aggregate interfacial transition zone. Different concrete mixes were used in fixed proportions along with varying concentrations of CNTs. The CNTs were applied in different concentrations, namely, 0.05 wt%, 0.1 wt% and 0.2 wt%, per dry weight. CNTs were dispersed using sonication. Concrete specimens were tested for compressive, flexural and split-tensile strengths. For each test, thirteen mix designs were investigated which included untreated aggregates and CNTs, and treated aggregates and CNTs. The results were compared with the results of the control concrete. The results showed that the use of CNTs improves the compressive, flexural and split-tensile strengths. It was concluded that CNTs minimize the ITZ.

Keywords. Multi walled carbon nanaotubes, interfacial transition zone, concrete, compressive strength, flexural strength, split-tensile strength, sonication

Introduction

Concrete is the most widely utilised material in the construction industry. However, concrete is generally very brittle and is characterized by a very low tensile strength and strain [1]. Tensile strength of concrete can be tested indirectly by flexural and split-tensile tests. Compressive strength of concrete is its indexing property as concrete has its maximum strength in compression. Concrete strength depends on various factors of which the ITZ is one variable. The Interfacial transition zone(ITZ) is a region in the concrete between the aggregate and hydrated cement paste. It is not a definite zone but rather a region of transition. The transition zone exits on a thin shell, typically 10-15μm thick around large aggregates. It is generally weaker than the other main components of concrete. This weaker zone can have an influence on the mechanical behaviour of concrete [2].

Nanotechnology is an emerging field of science and engineering. It is the new alternative of re-engineering concrete design and offers extraordinary environmental benefits. Nanotechnology promises significant enhanced material strength which is critical in constructions. Nano-materials improve particle parking capacity and concrete durability. According to Yamabe et al [3], CNTs were first synthesized in arc-discharge as a by-product of fullerene. There are two types of CNTs namely SWCNTs (single-walled carbon nanotubes) and MWCNTs. SWCNTs are synthesised under precisely controlled conditions in the presence of a catalyst.

[1]Corresponding author: pierrevt@uj.ac.za

In case of deviation from the production route of SWCNTs, MWCNTs are formed. They are made of 2 to 30 concentric graphic sheets (hexagonal, pentagonal or heptagonal) rolled into overlapping cylinders. Their diameters vary from 10 to 50nm and their length is greater than 10µm. CNTs have a modulus of elasticity of approximately 5 times higher, a tensile strength 100 times larger and elastic strain 60 times greater than steel. Tyson et al [1] performed an investigation using untreated and treated MWCNTs as reinforcement for cementitious materials. The samples were tested for both compression and flexural strengths. Treated CNTs produced compressive and flexural strengths respectively 2.7MPa and 0.4MPa higher than that of untreated CNTs.

Research by Ferro et al [4] shows that CNTs have a potential for crack bridging and enhanced stress transfer. Shah et al [5] investigated the effect of MWCNTs' length and concentration on the fracture properties of the nanocomposites with constant weight ratio. The fracture mechanics test results showed that the flexural strength of cement matrix significantly increased through the use of small amounts of MWCNTs (0.048 wt% and 0.08 wt%). In another study by Ximba [6], a series of compression tests were performed with different mix designs. The overall best mix design was found to be 0.2% treated aggregates and treated CNT. Luo [7] conducted a research on nanocomposites with different concentrations MWCNTs and different concentrations and combinations of surfactants. When comparing 0.5 wt% of MWCNTs to plain cement paste, it was found that pristine and annealed MWCNTs greatly improve flexural and compressive strengths. Reduced strength was achieved when using carboxyl functionalized MWCNTs.

1. Material properties and preparation

1.1 Material used

Table 1 lists the materials used to prepare the specimens. Material properties of the MWCNTs used are shown in Table 2.

Table 1. List of material used and their purposes

Material	Purpose
CEM IV 32.5R "Buildcrete" 13mm stone Washed crasher sand Fine sand Water	Standard concrete ingredients
MWCNTs	Reinforcement
Oil	Mould release agent

Table 2. Characteristics of the MWCNTs used

Property	Unit	Value	Method of Measurement
Average Diameter	Nanometers	9.5	TEM
Average length	Microns	1.5	TEM
Carbon Purity	%	90	TGA
Metal Oxide	%	10	TGA
Amorphous Carbon	-	Pyrolytically deposited carbon on the surface of the NC7000	HRTEM
Surface Area	m^2/g	250-300	BET

The following mix designs were used namely Control mix, Untreated aggregates and untreated CNT mix (UAUC), Untreated aggregates and treated CNT mix (UATC), Treated aggregates and untreated CNT mix (TAUC) and Treated aggregates and treated CNT mix (TATC). A total of 13 mix designs were investigated. Over 39 specimens were cast and tested.

1.2 Crypsination and sonication

Crypsination is a technology owned by Oxyfibre (Pty) Ltd. CNTs have a tendency to aggregate in an aqueous solution and repel water molecules. Crypsination is a process whereby aggregates and CNTs are treated to improve the bond between aggregates, CNTs and water. It is a gaseous process using fluorine as catalyst to modify the molecular structure on the surface of Polypropylene (or other exposed materials). The process renders the surface permanently wettable and adhesive. In the context of this study, treated aggregates and CNTs refer to crypsinated aggregates and CNTs, and untreated aggregates and CNTs refers to standard aggregates and CNTs.

For CNTs to be effectively utilized within materials, they must be properly dispersed. CNTs have a tendency to self-associate into micro-scale aggregate. Dispersion separates the bundles of CNTs into individual filaments within a matrix. Required amount of CNTs were sonicated for 30 minutes before mixing the solution with the concrete.

2. Experimental programme

2.1 Mixing of concrete and slump test

The amount of all required materials were weighed and measured. All the apparatus were cleaned and made ready. Stones and washed crusher sand were mixed for 2 minutes until the mixture had a uniform colour. The fines were added to the mixture and were mixed for a minute. Cement was added and mixed together with the mixture for 2 minutes. Sonicated solution of CNTs was added to the mixture in the drum and mixed for 5 minutes. The remaining amount of water required was further added and mixed until the concrete appeared homogeneous.

For all the concrete mixes prepared, slump tests were performed in accordance with SANS 5862-1:2006 standards [8]. All the tools were cleaned and wiped with a dump cloth prior to performing the slump test. The slump mould was placed on the steel plate with the narrow end at the top. With the two feet standing on the foot piece, the slump mould was filled with three layers of freshly mixed concrete. Each layer of about equal depth was tamped 25 times with a steel rod. After tamping the last layer, the excess concrete was stroked off with a steel rod. The slump mould was slowly lifted straight up and off. The distance between the bottom of the tamping rod and the highest point of the concrete was measured.

2.2 Moulding and curing of the specimens

The moulds were assembled and cleaned with a damp cloth. The internal surfaces of the moulds were coated with a thin layer of oil to prevent leakage of water through the joints and to prevent the adhesion of the concrete to the moulds [8,9]. During moulding, concrete was compacted using a steel rod to avoid honeycombing. Both beam moulds and cube moulds were filled with concrete in approximately 50mm layers. Each layer was stamped at least 45 times with the rod. A steel float was used to strike off excess concrete and to level the last layer. Each specimen was labelled and left overnight. The specimen were covered in a plastic sheet and stored in a cool place to avoid moisture loss.

After 24 hours, the specimens were removed from the moulds. The specimens were stored in a curing pond until they gained 28 days strength. The water in the curing pond was kept clean, at a temperature of ± 23°C.

2.3 Compression strength test

The compression test was performed according to the guidelines from SANS 5863:2006[10]. The cube specimens were taken out of the curing pond after 28 days. The surface water and grit were removed and the mass of the cubes were determined and recorded. Prior to testing, the bearing surfaces of the plates of the compression testing machine were wiped clean. The cube specimens were crushed one cube at a time. The cube in the machine was positioned to allow for the load to be applied on the opposite as-cast faces of the specimen. The corresponding cube mass and volume were entered on the data recording monitor and the load was gradually applied at the rate of 0.3MPa/s until the specimen failed. The maximum load applied was recorded and the appearance of the specimen was photographed. The compressive strength was calculated using the maximum failure load and the cross-sectional area of the specimen on which the compressive force acts.

2.4 Flexural strength test

Tensile strength is an important property of concrete because concrete structures are highly vulnerable to tensile cracking. Due to difficulty in applying uniaxial tension to concrete specimens, the tensile strength of the concrete is determined by indirect test methods, flexural and split-tensile tests. Only the flexural test was performed in the study and the split-tensile test was performed by another person and the results were used to analyse and evaluate the proposed mix designs. The flexural strength test was conducted on a computer controlled INSTRON compression testing machine with 250kN cell loader in the laboratory air atmosphere. The two-point loading method was used. The test was performed in accordance with SANS 5863:2006 [11]. The beam specimens were prepared similar to the cube specimens. A beam specimen was placed centrally on the supporting rollers. Prior to loading, it was ensured that the loading and supporting rollers are evenly in contact with the specimen. The load was applied uniformly without shock at the rate of 0.2mm/min until the bean specimen failed. The various applied loads together with the maximum failure load and deflections were recorded by the computer. The distance between the line of fracture and the position of the nearer supporting roller, along the centre-line of the bottom surface, was measured. The flexural strength was calculated using maximum failure load, the distance between the axis of the supporting rollers, the width and depth of the specimen.

2.5 SEM observations

A sample of about a cubic centimetre was extracted from the failed specimens for each mix design tested. The samples were left in the oven overnight to dry. The following day, the samples were taken out of the oven and were allowed to cool for 10 minutes. The samples were placed on the sample stubs/holders and were held in place by an adhesive tape. The coating process was performed in order to make the samples conductive. Most of the samples were coated twice due to poor electron conductivity. Gold coat was used because of irregular surface of the concrete samples. When coating process was completed, the samples were stored in the Glass Vacuum Desiccator until the SEM was available for use. The TESCAN Scanning Electron Microscope was used to observe the microstructure of various concrete samples. A high voltage of 20kV was used for most of the samples. An accelerating voltage of 10kV was used on some samples to reduce surface charging.

3. Results and discussion

3.1 Compressive strength test

The compression strength of each specimen was calculated using the Eq.(1).

.

$$f_{cc} = \frac{F}{A_c} \tag{1}$$

where f_{cc} = compressive strength (MPa); F = maximum load at failure (N); A_c = cross-sectional area of the specimen (mm^2).

The control mix had an average strength of 14.533. The average strength of the other mix designs, and the strength increase/reduction in comparison to the control mix design are shown in Table 3. Positive and negative percentages for the strength improvement respectively indicate an increase or decrease in strength.

From the results obtained, it was noted that the addition of 0.1 wt% TAUC, 0.05 wt% TATC and 0.1 wt% TATC greatly increased the compressive strength. The 0.05% UAUC, 0.1 wt% UAUC, 0.2 wt% UATC and 0.2 wt% TATC mix designs, reduced the compressive strength. This is as a result of poor dispersion and large amount of CNTs added.

Table 3. Average compressive strength and strength improvements for different mix designs

Mix Design	Concentration(%)	Average Strength(MPa)	Strength Improvement(%)
UAUC	0.05	13.617	-6
	0.1	14.347	-1
	0.2	15.711	8
TAUC	0.05	16.579	13
	0.1	18.056	20
	0.2	16.006	9
UATC	0.05	16.009	9
	0.1	16.692	13
	0.2	13.559	-7
TATC	0.05	17.751	18
	0.1	18.762	23
	0.2	13.121	-11

Figure 1 shows a graphical comparison of the mean compressive strengths from the different mix designs. A notable mix design is TAUC. It always yielded an increased compressive strength regardless of the concentration.

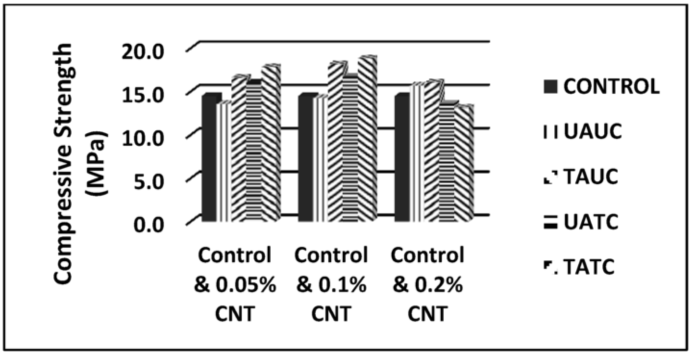

Figure 1. Comparison of average compressive strength per concentration of CNTs

Generally, 0.1 wt% concentration yielded an increased strength for almost all the different aggregate and CNTs combinations. The 0.05 wt% concentration produced moderate results. Poor results were achieved with 0.2 wt% concentration of CNTs. With high concentrations, the CNTs tend to self-associate into a micro-scale aggregates. This resulted in insufficient or poor dispersion. The more CNTs added, the less workable the concrete became. Concrete mixes with 0.2% CNTs concentration were very dry, hard to compact and mould by hand. These left voids within the concrete, thus weakening the strength of the specimens.

3.2 Flexural strength test

Eq. (2) was used to calculate the flexural strength of each specimen

$$f_{cf} = \frac{F \times \ell}{b \times d^2} \tag{2}$$

where f_{cf} = flexural strength (MPa); F = maximum load at failure (N); ℓ = distance between the axis of the supporting rollers (mm); b = width of the specimen (mm); d = depth of the specimen (mm)

According to SANS 5863 standards, the calculated results from Eq. (2) are considered valid only if the tension surface (bottom surface) is within the middle third of the span length[12]. All the results were considered valid because the lines of fracture were always between 100mm and 200mm for all the specimens.

The control mix had an average strength of 3.969. The average strength of the other mix designs, and the strength increase/reduction in comparison to the control mix design are shown in Table 4. Most mix designs on Table 4 show negative impact of CNTs on concrete flexural strength. Greatest improvement was found when 0.1 wt% concentration of untreated CNTs was added to treated aggregates. Addition of 0.2 wt% of treated CNTs to untreated aggregates produced the worst results.

Table 4. Average flexural strength and strength improvement for different mix designs

Mix Design	Concentration(%)	Average Strength(MPa)	Strength Improvement(%)
UAUC	0.05	3.619	-11
	0.1	4.371	8
	0.2	3.606	-11
TAUC	0.05	3.938	-2
	0.1	4.550	12
	0.2	3.683	-9
UATC	0.05	4.104	3
	0.1	4.486	11
	0.2	3.249	-23
TATC	0.05	4.420	10
	0.1	4.154	4
	0.2	3.623	-10

Graphical comparison of the different mixes per concentration is shown in Figure 2. Overall, 0.1 wt% of CNTs is the best concentration of the three. An improved flexural strength was achieved for all possible aggregate and CNTs combination for this concentration. The best mix design is 0.1 wt% TAUC with 4.7MPa average strength, and 12% strength increase. No improvement was shown when 0.2 wt% of CNTs was added to concrete. Only UATC and TATC showed an increase in flexural strength when 0.05 wt% of CNTs was used.

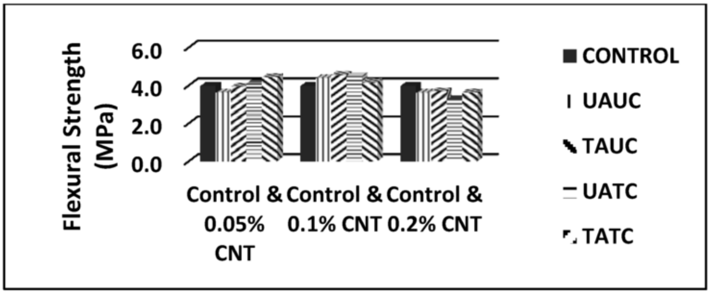

Figure 2. Comparison of average flexural strength per concentration of CNTs

3.3 Split-tensile test

Similar mix designs were considered and specimens were prepared the same way as the compressive and flexural tests. A total of 39 cylindrical specimens, with dimensions 300mm long and 150mm diameter were prepared.

Table 5. Average split-tensile strength and strength improvement for different mix designs

Mix Design	Concentration(%)	Average Strength(MPa)	Strength Improvement(%)
UAUC	0.05	1.359	26
	0.1	1.292	23
	0.2	1.215	18
TAUC	0.05	1.411	29
	0.1	1.213	18
	0.2	1.336	25
UATC	0.05	1.269	21
	0.1	1.456	31
	0.2	1.229	19
TATC	0.05	1.202	17
	0.1	1.296	23
	0.2	0.978	-2

Tables 5 shows the average strengths achieved for the different mix designs. The control mix had an average strength of 1.038MPa. The highest strength improvement achieved was 31% with the 0.1 wt% UATC mix design. Only 0.2 wt% TATC mix yielded a decreased strength.

The results in Table 5 were plotted as shown in Figure 3. The TAUC mix produced the highest strength when 0.05 wt% and 0.2 wt% concentrations of CNTs per dry weight were applied. When 0.1 wt% of CNTs was utilised, a combination of untreated aggregates and treated CNTs showed the greatest strength improvement.

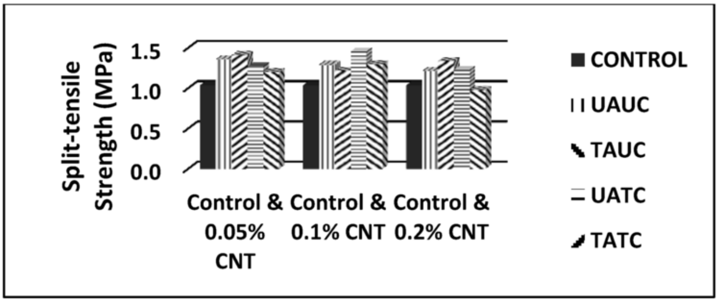

Figure 3. Comparison of average split-tensile strength per concentration of CNTs

3.4 SEM observations

The SEM was used to observe the impact the CNTs had on the ITZ. Figure 4 to 9 show micrographs of the fractured samples from four different mix designs.

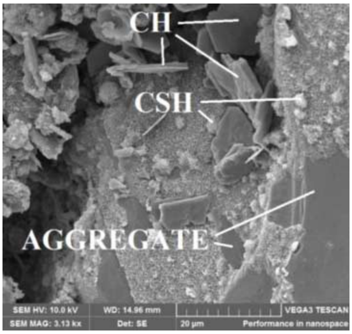

Figure 4. SEM image from the control mix

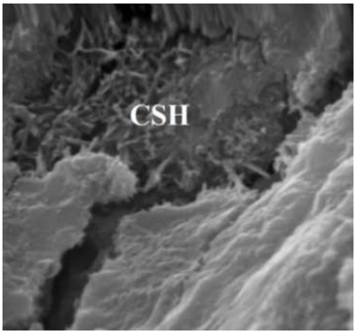

Figure 5. SEM image for 0.1% TATC, (mag: 2μm)

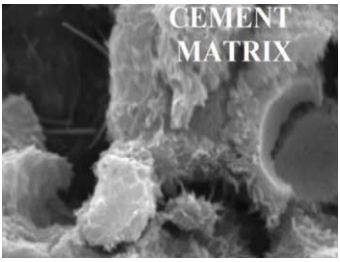

Figure 6. SEM image for 0.1% UATC sample (mag: 2μm)

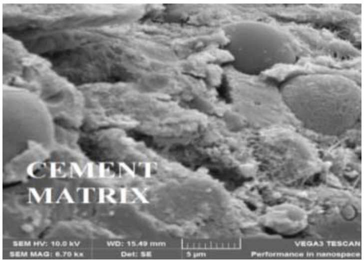

Figure 7. SEM image for 0.1% UAUC sample

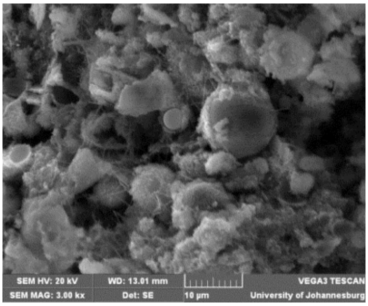

Figure 8. SEM image for 0.2% UAUC

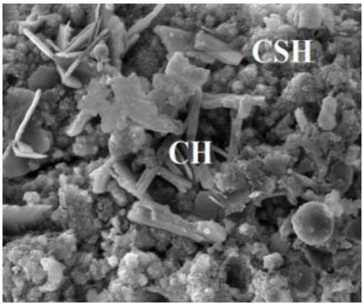

Figure 9. SEM image for 0.05% UATC sample (mag: 20μm)

The high concentration of CH is evident in the control sample in Figure 4. Other samples with reinforcement, were dominated by crystals of CSH and Ettringite. However, on some of the images it was not clear if the needle-like particles are the CNTs or the ettringite.

4. Conclusion

The CNTs improve the properties of concrete due to the effect the increased surface has on reactivity and through filling the micro- and nanopores of the ITZ. It was found that different concentrations of CNTs have different impacts on concrete strength. On average, the 0.1 wt% concentration improved the three tensile strengths better than 0.05 wt% and 0.2 wt% concentrations. When CNTs were applied in large amounts, the concrete lost its workability due to difficulty of nano-particles to disperse uniformly. These increased the voids within the concrete, leading to decreased strength especially the flexural strength.

Different combinations of treated and untreated aggregates and CNTs improved the concrete strength differently. The UATC and TATC combination worked well for most tests under different concentrations of CNTs. The overall best design mix is 0.1 wt% UATC. For compressive strength, 0.1 wt% TATC performed the best. For flexural strength, 0.1 wt% TAUC showed the greatest results, and 0.1 wt% UATC improved the split-tensile strength greatly.

During the SEM observation, it was hard to spot the CNTs because of similarities between CNTs and some of the concrete/cement particles such as Ettringite. The absence of CNTs in some samples was due to poor dispersion, and only a cubic centimetre samples were analysed. But the improved strengths achieved shows that CNTs bonded well with cement and this can possibly be because the ITZ was minimised. Further studies is under way to verify the position of these CNTs exactly. However, addition of large amount of CNTs worsened the voids because of poor workability and compaction. Though promising, several challenges have to be solved before introducing CNTs to the public through concrete technology. The challenges of using CNTs include: proper dispersion, high water demand, manufacturing methods, safety, handling issues and high costs.

References

[1] B.M. Tyson, Carbon nanotube and nanofiber reinforcement for improving the flexural strength and fracture toughness of portland cement paste. Texas: Texas A&M University, 2010.

[2] P.K. Mehta, P.J.M. Monterio, *Concrete: Structure, Properties, and Materials* (Prentice-Hall International Series in Civil Engineering and Engineering Mechanics). New York: Prentice-Hall International, 1993.

[3] T. Yamabe, K. Fukui, K. Tanaka., *The Science and Technology of Carbon Nanotubes*. Abiko City: Elsevier, pp. 2-11, 1999.

[4] G. Ferro, J.M. Tulliani, S. Musso, Carbon nanotubes cement composites. *The International Journal of the Italian Group of Fracture*, 18: 34-44, 2011.

[5] S.P. Shah, M.S. Konsta-Gdoutos, Z.S. Metaxa, Highly-dispersed carbon nanotube-reinforced cement based materials. Patent US 20090229494A1, 2009.

[6] S.I. Ximba, Procedures to eliminate aggregate interfacial transition zone. Johannesburg: University of Johannesburg, 2012.

[7] J.L. Luo, Fabrication and functional properties of multi-walled carbon nanotube/cement composites. *PhD thesis. Harbin: Harbin Institute of Technology*, 2009.

[8] SABS Standards SANS 5862-1:2006: Concrete tests - Consistence of freshly mixed concrete - Slump test. Pretoria: *SABS Standards Division*, 2006.

[9] SABS Standards SANS 5861-3:2006: Concrete tests - Part 3: Making and curing of test specimens. Pretoria: *SABS Standards Division*, 2006.

[10] SABS Standards SANS 5864:2006: Concrete tests - Flexural strength of hardened concrete. Pretoria: *SABS Standards Division*, 2006.

[11] K.L. Scrivener, A.K. Crumbie, P. Laugesen, The Interfacial Transition Zone (ITZ) Between Cement Paste and Aggregate in Concrete. *Interface Science*, 12: 411-421, 2004.